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US Appln No. 10/663,845  
Kawamura et al, Filed on 9/17/2003  
Confirmation No. 2854, Art Unit  
1773, Examiner Jackson, Monique

**STATEMENT**

I, Naoshi KITAMURA—of ARK Mori Building, 13F, 12-32, Akasaka 1-chome, Minato-ku, Tokyo 107-6013 Japan—hereby declare that I am conversant in both Japanese and English and that I believe the following is a true and correct translation of a certified copy of Japanese Patent Application No. 2002-277339.

Date: December 15, 2005

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PATENT OFFICE  
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this Office.

Date of Application: September 24, 2002

Application Number: Japanese Patent Application  
No. 2002-277339

Applicant: FUJI PHOTO FILM CO., LTD.

October 21, 2003

Commissioner, Patent Office Yasuo Imai (sealed)

Issuance No. 2003-3086484

(Designation of Document) Application for Patent

(Reference No.) P-42762

(Filing Date) September 24, 2002

(Addressed To) Commissioner, Patent Office

(International  
Classification) B01J 8/00

B01J 19/00

B41J 47/00

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(Indication of Fee)

(Deposit Account No.) 092740

(Amount) 21000

(List of Attached Documents)

(Article) Specification 1 copy

(Article) Abstract 1 copy

(General Power of attorney No.) 0003489

[Designation of Document] Specification

[Title of the Invention] FUNCTIONAL SURFACE MEMBER

[Scope of Claims for a Patent]

[Claim 1] A functional surface member comprising a support having a surface on which a graft polymer chain having a nonionic polar group in the side chain thereof is bonded and provided thereon a layer comprising adsorbed fine particles capable of bonding to the polar group.

[Claim 2] The functional surface member according to claim 1, wherein the fine particles capable of bonding to the polar group is fine metal particles.

[Detailed Description of the Invention]

[Technical Field to which the Invention belongs]

The present invention relates to a functional surface member. Particularly, the invention relates to a functional surface member having a functional surface layer comprising adsorbed various functional fine particles, for example, a roughened surface member, a conductive member and a light shielding member.

[Related Art]

Various members having a surface layer with various functions prepared by adsorbing functional fine particles on appropriate substrates have been proposed. Examples of the member having a fine particle-adsorbed surface layer include anti-reflection members with irregularity formed by fine metal

particles, conductive members having conductive fine particles adsorbed thereon, anti-staining and antibacterial members having antibacterial metal (or metal oxide) adsorbed thereon, gas barrier films reducing gas permeability by utilizing fine particle-laminated structure and light shielding members using fine particle materials shielding ultraviolet ray, infrared ray or visible light.

As typical examples thereof, the roughened surface members having the specified fine irregularity are useful as materials for controlling the refractive index at an interface to prevent light reflection.

In recent years, image displays as typified by liquid crystal display (LCD), plasma display (PDP), cathode ray tube display (CRT) and electroluminescence (EL)-lamp have been used increasingly in various fields, for example, television sets, computer machines and various mobile units which are becoming widespread recently. Such image displays have made prominent progresses. With improvement of the functions of various units using the displays, the demands of high-quality imaging and low electricity consumption toward the displays are increasing. For the high-quality imaging, anti-reflection property preventing reflection of light such as illumination on the display surface is an important element, along with the improvement of the pixel density in images and the achievement of bright color tone.

Particularly, since it is expected that displays for portable terminals which are becoming more widespread lately be obviously used outdoors, the demand of strong anti-reflection property preventing reflection of exterior light such as sunlight or fluorescent light on the display is increasing more than ever.

Additionally, LCDs of lightweight, compact size and versatility are broadly used. In the mobile units (portable terminals), the touch-panel input mode, namely an operation mode with direct touching of predetermined areas on the display surface with a plastic pen or fingers is frequently used. Not only image quality and anti-reflection property but also properties, for example, durability such as abrasion resistance and anti-staining property are now important for the display surface.

For the prevention of reflection, an approach to roughening the incident surface so as to scatter or disperse light has been ordinarily made in the related art. Treatment for roughening the surface include, for example, a roughening method of substrate surface directly with a sandblast process or an emboss process and a method for providing a surface roughened layer by coating a coating solution containing fillers on the substrate surface and drying.

Among them, the method for providing a surface roughened layer containing fillers on the substrate surface is commonly used currently from the standpoint of the controllability of

the dimensions of irregularity on the surface to be roughened and the easy production of surface roughened layer.

For example, patent reference 1 (JP-A-6-18706) proposes a surface roughened layer comprising a UV-curing resin and a resin bead for the purpose of applying to highly transparent plastic film with poor thermal resistance.

A proposition using an inorganic pigment having good abrasion resistance such as silica instead of the resin bead is also made. However, such inorganic pigment is disadvantageous in its dispersibility, thereby causing a problem that a uniformly roughened surface layer is hardly produced. Therefore, for example, patent reference 2 (JP-A-11-287902) proposes a surface roughened layer using two kinds of pigments comprising silica and a resin filler having good dispersibility.

However, any one of these methods is a method of forming a surface roughened layer by coating filler for forming irregularity with a binder on a substrate. Therefore, the method has potentially a problem in that the level of the irregularity formed from the filler is reduced upon the influence of the binder, so that the anti-reflection property at the level as planned is hardly obtained. Further, when the binder is diluted or the amount of binder used is reduced for the purpose of improving the effect of filler on the irregularity, the strength of the resulting film is deteriorated so that it is likely to cause a problem of the durability.



As another method for forming an anti-reflection layer, a method of laminating alternately a material of a large refractive index and a material of a small refractive index to form a multi-layer construction is known. Specifically, the method for forming a multi-layer construction includes a vapor phase process of forming a film including alternately depositing a material of a small refractive index as typified by  $\text{SiO}_2$  and a material of a large refractive index such as  $\text{TiO}_2$  or  $\text{ZrO}_2$  and a sol gel process using hydrolysis and condensation polymerization of metal alkoxide.

Regarding these methods for forming anti-reflection layer of multi-layer construction, the vapor phase process using deposition requires a costly processing apparatus and involves difficulty in the production of anti-reflection layer of large size, while the sol gel process requires high production costs because of the repetition of the coating and baking procedures and additionally involves a problem in that stain is noticeable on the resulting anti-reflection layer because the anti-reflection layer is colored purple or greenish.

Patent Reference 1: JP-A-6-18706

Patent Reference 2: JP-A-11-287902

[Problems that the Invention is to Solve]

In light of the disadvantages of the related art as described above, it is an object of the invention to provide a functional surface member, which has a fine particle-adsorbed

layer excellent in durability comprising functional fine particles strongly adsorbed on the surface in the form of a single layer or a laminate layer, and in which the effect of the functional fine particles adsorbed is sustainable.

Another object of the invention is to provide a functional surface member having the properties described above, wherein a fine particle-adsorbed layer of a multi-layer construction is readily formed.

[Means for Solving the Problems]

The above-described objects of the invention are attained by a functional surface member comprising a support having a surface on which a graft polymer chain having a nonionic polar group in the side chain thereof is bonded and provided thereon a layer comprising adsorbed fine particles (particularly, fine metal particles) capable of bonding to the polar group.

The mechanism of the invention is not definitely clear. In accordance with the invention, however, polar groups are introduced onto a surface of a support and a layer composed of uniformly filled in the high density with fine particles, which have properties capable of bonding with the polar group upon the polar interaction therebetween, for example, functional fine metal particles, e.g., fine particles of metal oxide is formed on the surface of the support. Consequently, a surface layer of the fine particles is formed without using a binder. Specifically, a fine particle-adsorbed layer reflecting the

shape of fine particle or the function of fine particle as it is, for example, a surface roughened layer having uniform irregularity, or a functional surface layer, e.g., a conductive layer of conductive fine particles is formed. The surface layer can exert excellent functions. It is assumed that since the polar groups on the surface and the fine particles capable of adsorbing the polar groups are strongly adsorbed each other upon the polar interaction, the abrasion resistance is enhanced, so that the fine particle-adsorbed layer exhibits high durability.

The presence of the fine particle-adsorbed layer having such construction is recognized apparently by observing the surface using an atomic force microscope (AFM) or by observing the cross section using a scanning electron microscope. Specifically, the ~~structure~~ structure of the layer is confirmed based on the formation of fine irregularity on the surface or the formation of laminate of fine particles. It is also possible to confirm the presence of the functional layer composed of fine particles by measuring the properties derived from the functional fine particles.

[Mode for Carrying Out the Invention]

The invention is described in detail below.

In the functional surface member of the invention, a graft polymer chain with a nonionic polar group in a side chain thereof exists on at least one face of the support. Generally, the surface with such polar group is preferably prepared by surface

grafting process. So as to obtain an optical transmission member such as anti-reflection film and infrared absorption film, a transparent substrate is preferably used as the substrate of the support.

[Substrate with polar group introduced onto the surface]

The surface bound to a graft polymer chain with a nonionic polar group in a side chain thereof is prepared by surface grafting process of grafting a monomer with a nonionic polar group in a side chain thereof onto a surface of a substrate by known techniques with light, electron beam and heat or of binding a macromer or a polymer with a nonionic polar group in a side chain thereof onto the surface of a support to prepare the surface with the polar group. Further, the polar group preferably includes nonionic polar groups with hetero atoms, specifically nitrogen atom, sulfur atom and oxygen atom. Additionally, the nonionic polar group with such hetero atoms includes hetero aromatic groups with nitrogen atom and sulfur atom, such as pyridine group, quinoline group, thiophene group and benzothiophene group; amino groups such as dimethylamino group and diethylamino group; ether groups and thioether groups containing oxygen atom or sulfur atom, such as ethyleneoxy group and thioethyleneoxy group; or lactone groups such as butyrolactone and lactam groups such as pyrrolidone.

As a method for introducing a graft polymer chain with a nonionic polar group in a side chain thereof onto a support

such as film substrate, specifically, descriptions in for example "Surface Modification with Macromonomer and Adhesion" by the author Shinji Sugii in "Japanese Rubber Association Journal", 1992, Vol.65, p.604 can be referenced. Additionally, the process called surface graft polymerization process described below can also be applied.

The surface graft polymerization process is a process for synthetically preparing graft polymer including giving an active species onto the chain of a polymer compound to thereby start the polymerization of a different monomer. When the polymer compound given the active species forms a solid surface, the process is particularly called surface graft polymerization.

As the surface graft polymerization process for practicing the invention, any known method described in references can be used. For example, "New Polymer Experimental Lecture 10", edited by Polymer Association, Kyoritsu Shuppan (KK.), 1994, p.135 describes optical graft polymerization process and plasma irradiation graft polymerization process as the surface graft polymerization process. Additionally, "Adsorption Technique Manual", supervised by Takeuchi, NTS (KK.), February 1999, p.203 and p. 695 describes a graft polymerization process under irradiation of radiation including  $\gamma$  ray and electron beam.

As specific procedures for optical graft polymerization process, procedures described in JP-A-63-92658, JP-A-10-296895 and JP-A-11-119413 can be used.

Besides the processes, the method for preparing surface with surface grafted polymer includes a process of giving reactive functional groups such as trialkoxysilyl group, isocyanate group, amino group, hydroxyl group and carboxyl group to the terminus of the chain of a polymer compound, for coupling reaction with a functional group on the substrate surface. In recent years, additionally, the use of atomic transfer radical polymerization process as the surface graft polymerization process has been started. It has been found that the use of the process enables the preparation of bonds on the graft polymer surface at a high density. The polymerization process can be carried out with reference to K. Matyjaszewski, et al., "Polymer Preprints", 2000, Vol.41, p. 411; M. L. Bruening, et al., "J. Am. Chem. Soc.", 2000, Vol.122, p.7616; and "Macromolecules", 2002, Vol.35, p.1175.

Specific examples of the monomer with a nonionic polar group, which contains hetero atoms such as sulfur and oxygen, include 4-vinylpyridine, 2-vinylpyridine, N-vinylpyrrolidone, N,N-dimethylaminoethyl (meth)acrylate, N-morpholinoethyl (meth)acrylate, methoxydiethylene glycol (meth)acrylate, methoxypolyethylene glycol (meth)acrylate,  $\gamma$ -butyrolactone (meth)acrylate and mevalonic lactone (meth)acrylate.

In case that the functional surface member herein obtained is to be used as a surface roughened member for anti-reflection

materials for image displays with high-density pixels for high resolution and image displays of a small type for use in mobile units and with high resolution, a transparent substrate with smooth surface is preferably used so as to control the surface recess and protrusion shapes to be formed. So as to improve the macroscopic anti-reflection potency, the substrate surface may preliminarily be roughened for the purpose of enlarging the surface area to introduce numerous ionic groups (nonionic polar groups??) .

As the method for roughening the substrate, known processes suitable for the material of the substrate can be selected. In case that the substrate is resin film, for example, the method specifically includes glow discharge process, sputtering process, sandblast polishing process, buff polishing process, particle deposition process and particle coating process. In case that the substrate is a metal plate such as aluminium plate, additionally, a mechanically roughening process, a process of electrochemically dissolving and roughening surface and a process of chemically dissolving surface in a selective manner are applicable. As mechanical processes, known processes can be used, such as ball polishing process, brush polishing process, blast polishing process and buff polishing process. The electrochemical roughening process includes a process in an electrolyte of hydrochloric acid or nitric acid via alternate current or direct current. Further,

a process of any combination of the two electrolytes with the two current types may also be used.

[Fine particle interactive with polar group to bind to polar group]

1. Fine particle

Next, the fine particle capable of binding to the polar group is described. The fine metal particle to be used is selected appropriately, depending on the intended use of the functional surface. The metal herein referred to includes elements such as transition metals, alkali metals, alkali earth metals and metal elements of aluminum and silicone and includes not only simple metal substances but also metal compounds such as metal oxides. Because the resulting fine particle is adsorbed via the polarity, the particle size of the fine particle and the adsorbed amount thereof are limited. Generally, the particle size is within a range of preferably 0.1 nm to 1  $\mu$ m, more preferably 1 nm to 300 nm, and particularly preferably 5 nm to 100 nm.

In accordance with the invention, the particle-capable of binding to the graft interface via the interaction is regularly arranged at an almost monolayer state or is arranged at laminate states as the consequence of the adsorption of each nano-scale metal fine particle onto the individual polar groups in the long graft chain.

The fine metal particle functional for use in the invention



is now described, in a manner dependent on the intended use of the functional surface member.

#### 1.1 Fine metal particle for anti-reflection member

In case that the functional member of the invention is to be used as an anti-reflection member, preferably, at least one fine metal particle selected from fine particles of metal oxides is used as the functional fine metal. By using such fine particle, a surface roughened member can be provided, which is preferably used as an anti-reflection member preferable for use on the surface of image display, having uniform and great anti-reflection potency to produce sharp images with no deterioration of image contrast and being capable of achieving excellent durability.

The fine particles of metal oxides preferably include silica ( $\text{SiO}_2$ ), titanium oxide ( $\text{TiO}_2$ ), zinc oxide ( $\text{ZnO}$ ) and tin oxide ( $\text{SnO}_2$ ). Further, fine particles of pigments including so-called transparent pigments and white pigments, such as calcium carbonate, aluminium hydroxide, magnesium hydroxide, clay and talc can be used alike, when the fine particles have preferable shapes as described below.

For the use, the particle size of the fine particle is within a range of preferably 100 nm to 300 nm, more preferably 100 nm to 200 nm. In this mode, the particle binding via the ionic strength to the graft interface is regularly arranged at an almost monolayer state. In case that the surface roughened

member of the invention is to be used as an anti-reflection member and in view of the effect, the film thickness is controlled to  $\lambda/4$  provided that  $\lambda$  is the wavelength at which reflection is to be prevented. In light of the fine particle size almost equal to the film thickness of the surface roughened layer, the anti-reflection potency is likely lowered because of the too thin thickness of the surface roughened layer, when the particle size is less than 100 nm. When the particle size is more than 300 nm, further, the dispersion and reflection is large to cause significant opacity, so that it is hard to get transparency and the contact area binding to the graft interface via the polar strength is too small so that the strength of the surface roughened layer tends to be reduced.

#### 1-2. Fine particle for conductive film

In case that the functional member of the invention is to be used as a conductive film, at least one fine particle selected from fine metal particles, fine particles of metal oxides and fine particles of metal compounds, conductive or semiconductive, is preferably used.

The conductive fine metal particles or the fine particles of metal oxides include any diverse conductive metal compound powders of a specific resistance of  $1000 \Omega \cdot \text{cm}$  or less. Specifically, they include for example powders of simple substances of silver (Ag), gold (Au), nickel (Ni), copper (Cu), aluminium (Al), tin (Sn), lead (Pb), zinc (Zn), iron (Fe),

platinum (Pt), iridium (Ir), osmium (Os), palladium (Pd), rhodium (Rd), ruthenium (Ru), tungsten (W) and molybdenum (Mo) and their alloys thereof. Additionally, powders of tin oxide ( $\text{SnO}_2$ ), indium oxide ( $\text{In}_2\text{O}_3$ ), indium tin oxide (ITO) and ruthenium oxide ( $\text{RuO}_2$ ) may also be used.

Still additionally, particles of metal oxides and metal compounds with semiconductor properties may also be used and include for example fine particles of oxide semiconductors such as  $\text{In}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{ZnO}$ ,  $\text{CdO}$ ,  $\text{TiO}_2$ ,  $\text{CdIn}_2\text{O}_4$ ,  $\text{Cd}_2\text{SnO}_2$ ,  $\text{An}_2\text{SnO}_4$ ,  $\text{In}_2\text{O}_3\text{-ZnO}$  and fine particles using members doped with impurities suitable for them and additionally include for example fine particles of spinel-type compounds such as  $\text{MgInO}$  and  $\text{CaGaO}$ , fine particles of conductive nitrides such as  $\text{TiN}$ ,  $\text{ZrN}$  and  $\text{HfN}$ , and fine particles of conductive borides such as  $\text{LaB}_6$ . These may be used singly or a mixture of two or more thereof.

#### 1-3. Fine metal particle for antibacterial surface material

In case that the functional member of the invention is to be used as an antibacterial material, fine metal particles with antibacterial function and bactericidal function are preferably used as the functional fine particle.

The material capable of forming such fine metal (metal compound) particle specifically includes for example simple metal substances with bactericidal function, such as silver (Ag) and copper (Cu), alloys containing at least one of such simple metal substances, or metal oxides thereof. Further, the member

includes semiconductors of metal compounds with bactericidal action under irradiation of light at wavelengths in the ultraviolet region, such as florescent lamp and sunlight, which is for example titanium oxide, iron oxide, tungsten oxide, zinc oxide and strontium titanate, and metal compounds prepared by modification of these metal compounds with platinum, gold, palladium, silver, copper, nickel, cobalt, rhodium, niob and tin.

#### 1-4. Fine particle for ultraviolet absorbing member

In case that the functional member of the invention is to be used as an ultraviolet absorbing member, the use of fine particles of metal oxides such as iron oxide, titanium oxide, zinc oxide, cobalt oxide, chromium oxide, tin oxide and antimony oxide as the functional fine particle is preferable because the metal oxides have high shielding function in the ultraviolet regions A & B (wavelength at 280 nm to 400 nm). In accordance with the invention, a composite is prepared from the functional member by using a polymer compound as a substrate, which exerts high function and processability as an ultraviolet shielding film and sheet and promises various applications. Further, it is expected that the light resistance of polymer materials can be modified, by using the ultraviolet shielding effect of the metal oxides.

#### 1-5. Fine particle for optical material

The functional fine particle for use in color filter,

sharp cut filter and non-linear optical materials used in optical machines includes fine particles of semiconductors such as CdS and CdSe or metals of gold and the like. By using as the substrate silica glass or alumina glass, the resulting product can be used preferably as color filter. Additionally, the product may be used for non-linear optical materials such as optical switch and optical memory materials owing to the verification that the product has a large three-dimensional optical non-linear sensitivity ratio. The fine particle to be used herein specifically includes rare metals such as gold, platinum, silver and palladium or alloys thereof. From the standpoint of stability, substances never rapidly dissolving with alkali, for example gold and platinum, are preferably included.

Further, ultra-fine particles of ~~metals~~ (metal compounds) preferable as non-linear optical materials specifically include for example simple substances of gold (Au), silver (Ag), copper (Cu), platinum (Pt), palladium (Pd), rhodium (Rh), osmium (Os), iron (Fe), nickel (Ni) and ruthenium (Ru) and alloys containing at least one of them, which should be of a mean particle size of 10 to 1,000 angstroms. Additionally, the particle size is of a primary particle or a secondary particle. Preferably, however, the particle size never scatters visible light. Among them, fine particles of rare metals selected from Au, Pt, Pd, Rh and Ag or metals selected from Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd, Y, W, Sn, Ge, In and Ga are preferably included,

after they are independently dispersed in solvents such as toluene and they are of a particle size of 10 nm or less.

In case that a non-linear optical material is to be prepared using these ultra-fine particles by general methods, i.e. sol-gel process, immersion process, sputtering process, ion injection process or melting deposition process, the ultra-fine particles very readily aggregate, disadvantageously causing difficulty in the increase of the concentrations of the particles in the composite or the reduction of the productivity. Particularly, such ultra-fine particle at a low concentration and at a small contribution ratio to physical properties has limited uses and is unsuitable for image memory and optical integrated circuit utilizing the three-dimensional non-linear optical effect. According to the constitution of the invention, the fine particle is directly bound via the ionic strength (polarity?? polar strength??) to the ionic group (nonionic polar group??) on the substrate surface, and the nonionic polar group exists at a high density via grafting. Therefore, the concentration of the fine particle can readily be increased. The ultra-fine particle is particularly preferable for use in such non-linear optical material among optical materials.

#### 1-6. Fine particle for gas barrier film

In case that the functional surface member of the invention is to be used as a gas barrier film, the functional fine particle preferably includes ultra-fine particles of inorganic compounds

of silicone oxide, zirconium oxide, titanium oxide, alumina, magnesium oxide and tin oxide and ultra-fine particles of metals such as aluminium, tin and zinc, which are of a mean particle size of 100 nm or less, preferably 50 nm or less. As the ultra-fine particle, at least one selected from the ultra-fine particles of the inorganic compounds or of the metals is used singly. Otherwise, two or more thereof selected from them can be used in a mixture. By using an insulating inorganic compound such as silicone oxide as the ultra-fine particle, the entirety of the functional member can get insulating property. The ultra-fine particle is preferably an ultra-fine particle of silicone oxide, because silicone oxide is particularly readily prepared into ultra-fine particle.

As the substrate, further, it is preferable to use organic resin films with high gas barrier property, such as polyethylene terephthalate, polyamide, polypropylene, ethylene-vinyl alcohol copolymer and polyvinyl alcohol.

Application examples of the functional surface member of the invention and specific examples of the fine metal particle preferably used in the fields have been described insofar, but these never limit the invention. Selecting a substrate with an introduced polar group on at least one face of the substrate and a fine metal particle type with physico-chemical properties based on which the fine metal particle can be bound to the polar group to thereby make an appropriate combination, various members

with functional surface can be constructed, by actively utilizing the physico-chemical properties of the functional fine particle. [Adsorption of fine particle onto polar group]

In a specific mode of adsorption, the graft polymer chain of polyvinyl pyridine is introduced onto the surface of a support by using a nonionic monomer, for example pyridine group as the polar group, and then, the resulting substrate is immersed in a dispersion solution of fine silica particle for a given period of time. Subsequently, the excess of the dispersion solution is rinsed off with a solvent, to thereby form a fine particle-adsorbed layer with the fine silica particle adsorbed at a high density on the surface of the transparent substrate.

In such manner, a fine metal particle-adsorbed layer with a desired function can be arranged on a support substrate by introducing a polar group onto the support substrate and allowing the support substrate to adsorb the fine particle. The film thickness of the fine metal particle-adsorbed layer is selected, depending on the intended use. Generally, however, the film thickness thereof is within a range of preferably 1 nm to 1  $\mu$ m, more preferably 10 nm to 0.5  $\mu$ m. When the film thickness is too thin, the abrasion resistance is likely to be reduced. When the film thickness is too thick, the transparency is likely to be reduced.

(Substrate)

The support substrate to be used for forming a surface



with a graft polymer chain with a nonionic polar group in a side chain thereof is any plate-like substance dimensionally, which can satisfy the required flexibility, strength and durability and the like. In case that a transparent substrate is to be selected due to the requirement of optical transparency, the transparent substrate includes for example glass plate, quartz plate, plastic film (made of for example cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose butyrate, cellulose acetate butyrate, cellulose nitrate, polyethylene terephthalate, polyethylene, polystyrene, polypropylene, polycarbonate, polyvinyl acetal) and the like. The substrate for functional surface member with no need of transparency includes for example silicone plate, paper, plastic-laminated paper, metal plate (for example, plates of aluminium, zinc, copper and the like), and paper or plastic film laminated or deposited with metals as described above, in addition to those described above.

These are appropriately selected, depending on the relation between the use and the adsorbed fine particle. In view of processability and transparency, a substrate with a surface made of a polymer resin is preferable. Specifically, resin films, transparent inorganic substrates with resin-coated surface such as glass, and composite materials with surface layers made of resin layers are all preferable.

The substrate with resin-coated surface typically

includes for example laminate plates with resin film-attached surface, primer-treated substrates and hard coat-treated substrates. The composite materials with surface layers made of resin layers typically include for example resin seal materials with an adhesive layer on the back face, and laminate glass as a laminate material of glass and resin.

On the functional surface member of the invention is formed a layer of fine particles with specified functions such as fine particles of metal oxides typically including silica as uniformly adsorbed via electrostatic function at high densities onto a polar group introduced onto the substrate. Because a surface layer of the fine particles adsorbed in a monolayer state or a multi-layer state onto the polar group is formed with no use of any binder, the surface works as a functional surface reflecting the physico-chemical properties of the fine particles as they are. In case that fine particles for surface roughened member are used as the fine particles, for example, a surface roughened layer with a uniform shape made of the fine particles in recess and protrusion and with uniform and dense recesses and protrusions is formed. In case that the surface roughened member is used as an anti-reflection material, further, the layer of itself is a thin layer although the layer can achieve high anti-reflection potency. When a transparent substrate is used as the substrate, additionally, no concerns about the damage of optical transparency exist. Therefore, the functional

surface member of the invention can preferably be used not only for reflection type image display but also for transparent type image display.

The fine particle-adsorbed layer capable of reflecting the characteristic properties of the functional fine particles when appropriately selected can be formed on an appropriate substrate surface by relatively simple treatment. Additionally because the durability of the fine particle-adsorbed layer capable of exerting great function is high, advantageously, the functional surface member of the invention can be used preferably for diverse uses as described above.

The uses are further exemplified. Via selection of fine metal particles, the resulting functional surface can exert various functions such as electronic and electric functions given to a functional surface by using a conductive inorganic fine particle when selected; magnetic functions given to a functional surface by using a magnetic fine particle such as ferrite particle when selected; and an optical function by using a fine particle absorbing, reflecting or scattering light at a specified wavelength. The functional member can be used in wide fields such as various industrial products, pharmaceutical products, catalysts, varistors (variable resistors) and paints. In addition to these various and diverse functions of various materials composing the fine particles, the use of a polymer material as the substrate enables the use of the ready mold

processability of the polymer material, which promises the development of a novel material.

Specific examples of the use in wide fields include diverse uses including optical parts; sunglass; shield film, shield glass, shield window, sunproof container and sunproof plastic bottle against light such as ultraviolet ray, visible light and infrared ray; antibacterial film; microorganism- disinfected filler; antibacterial plastic mold articles; fishery network; various OA machines and home electronic machines such as television set parts, parts for telephone set, OA machine parts, vacuum cleaner parts, electric fan parts, air conditioner parts, refrigerator parts, washing machine parts, humidifier parts and dish washer parts; or sanitary products such as toilet seat parts and wash hand basin parts; other building materials; automobile parts; daily products; toys; and miscellaneous items.

[Examples]

The invention is more specifically described in the following examples, which never limit the invention.

(Example 1)

Preparation of substrate A with surface graft polymer

[Preparation of surface polyvinyl pyridine graft by atomic transfer radical polymerization]

In argon stream, a glass plate thoroughly rinsed was immersed in 1 % solution of 5-(trichlorosilylpentyl)-2-bromo-2-methylpropionate (the

initiator terminal silane coupling agent) in toluene. After immersion overnight at ambient temperature, the glass plate was taken out and rinsed with toluene and methanol to obtain the glass plate with the initiator terminal silane coupling agent immobilized thereon. Herein, the initiator terminal silane coupling agent 5-(trichlorosilylpentyl)-2-bromo-2-methylpropionate was synthetically prepared by the method described in the reference (see C. J. Hawker et al., *Macromolecules*, 1999, Vol.32, p.1424).

Then, a solution was prepared by dissolving 4-vinylpyridine (47.7 g), cuprous bromide (0.646 g) and tris-(2-dimethylaminoethyl)amine (1.0 g) in isopropanol (100 ml), followed by purging with argon stream for 15 minutes for deaeration. The glass plate with the initiator terminal silane coupling agent immobilized thereon was immersed in the solution at ambient temperature. After immersion for one hour, the glass plate was taken out and rinsed with water and methanol. Then, the surface of the glass plate was rubbed with a cloth (BEMCOT) impregnated with methanol. The film thickness was measured by ellipsometry (VB-250 manufactured by J. A. Woolam Co., Ltd.). Grafting at a film thickness of 10 nm was confirmed.

[Fine particle of metal oxide capable of interacting with polar group]

In the present Example,  $\text{TiO}_2$  particle was used as the fine particle of metal oxide.

[Particle adsorption onto substrate]

Substrate A with the surface graft polymer was immersed in a dispersion solution of a  $\text{TiO}_2$  dispersion (5 g) [H40; manufactured by Tagi Kagaku KK.] and water (5 g) for 20 minutes. Subsequently, the surface was thoroughly rinsed with tap water, to remove the excess of the aqueous dispersion solution of the fine particle, to obtain surface roughened member B with a surface roughened layer via fine particle adsorption on the surface thereof.

The surface of the surface roughened member B was observed with a transmission type electron microscope (JEOL JEM-200CX) at  $\times 100,000$ . It was verified that dense recessed and protruded shapes due to the fine particle were formed.

[Evaluation of anti-reflection potency]

The ratio of the reflecting beam flux  $\phi_r$  to the incident beam flux  $\phi_i$  ( $\phi_r/\phi_i$ ) on the surface of the surface roughened member, namely the visibly appreciated reflection ratio (%) was measured with a spectrometer. The reflection ratio of the surface roughened member B was 0.2 %. It was thus confirmed that the surface roughened member B had great anti-reflection potency.

[Evaluation of abrasion resistance]

The resulting surface roughened member B was rubbed with a cloth (BEMCOT; manufactured by Asahi Kasei KK.) moistened with water by hands thirty times in a reciprocal fashion. After

rubbing, the surface thereof was observed with the transmission type electron microscope (JEOL JEM-200CX) at  $\times 100,000$ . It was then verified that dense recessed and protruded shapes due to the fine particle like the shapes observed before rubbing were observed and the dense recessed and protruded shapes on the surface were not damaged even through rubbing.

(Example 2)

In the present Example,  $\text{SiO}_2$  particle was used as a fine metal oxide particle.

[Particle adsorption onto substrate]

Substrate A with the surface graft polymer as prepared in Example 1 was immersed in a dispersion solution of a silica particle of a mean particle size of 200 nm (10 g) [Sea holster; manufactured by Nippon Shokubai, Co., Ltd.] in cyclohexane (90 g) for 20 minutes. Subsequently, the surface was thoroughly rinsed with acetone and tap water, to remove the excess of the dispersion solution of the fine particle, to obtain surface roughened member C with a surface roughened layer.

The surface of the surface roughened member C was observed with a transmission type electron microscope (JEOL JEM-200CX) at  $\times 100,000$ . It was verified that dense recessed and protruded shapes due to the fine particle were formed.

The anti-reflection potency and abrasion resistance of the resulting surface roughened member C were evaluated as in Example 1. The visibly appreciated reflection ratio was 0.2 %.

Even after rubbing, there was no observed change of the recessed and protruded shapes on the surface. Hence, it was found that high anti-reflection potency and surface abrasion resistance were also achieved in this Example with the cationic surface.

The results of the evaluation of these Examples indicate that the functional surface member of the invention exerts great performance corresponding to the functions of the fine particles adsorbed and has such highly durable fine particle-adsorbed layer formed on the surface. Therefore, the functional surface member of the invention is useful for materials with various functional surfaces suitable for practical use.

#### [Advantage of the Invention]

In accordance with the invention, a functional surface member, which has a fine particle-adsorbed layer excellent in durability comprising functional fine particles strongly adsorbed on the surface thereof and in which the effect of the fine particles adsorbed is sustainable, can be provided.



[Designation of Document] Abstract

[Abstract]

[Problem] To provide a functional surface member with a fine particle-adsorbed layer with great durability, where the effect of the functional fine particle adsorbed is sustainable, as produced by allowing a functional fine particle to be adsorbed strongly in a monolayer or a laminate state onto the surface.

[Means for Resolution] A functional surface member comprising a support having a surface on which a graft polymer chain having a nonionic polar group in the side chain thereof is bonded and provided thereon a layer comprising adsorbed fine particle capable of polarly bonding to the polar group.

[Selected Drawing] None

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